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# Diamond and Diamondlike Carbon as Wear-Resistant, Self-Lubricating Coatings for Silicon Nitride

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# DIAMOND AND DIAMONDLIKE CARBON AS WEAR-RESISTANT, SELF-LUBRICATING COATINGS FOR SILICON NITRIDE

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Recent work on the friction and wear properties of as-deposited fine-grain diamond, polished coarse-grain diamond, and as-deposited diamondlike carbon (DLC) films in humid air at a relative humidity of approximately 40 percent and in dry nitrogen is reviewed. Two types of chemical vapor deposition (CVD) processes are used to deposit diamond films on silicon nitride ($Si_3N_4$) substrates: microwave-plasma and hot-filament. Ion beams are used to deposit DLC films on $Si_3N_4$ substrates. The diamond and DLC films in sliding contact with hemispherical bare $Si_3N_4$ pins have low steady-state coefficients of friction (< 0.2) and low wear rates (< $10^{-7}$ $mm^3/N{\cdot}m$), and thus, can be used effectively as wear-resistant, self-lubricating coatings for $Si_3N_4$ in the aforementioned two environments.

Keywords: Diamond film, DLC film, Tribology, Wear, Friction

## 1. INTRODUCTION

Structural ceramics such as $Si_3N_4$ and silicon carbide (SiC) are frequently the materials of choice in engine components, tools, and wear parts, such as turbine rotors, cutting tools, dies, mechanical-face seals, and rolling-element bearings. However, structural ceramics lack inherently good friction and wear properties. Clearly, what is needed is a means to provide acceptable levels of friction and wear properties for structural ceramics. Presently, liquid lubrication or some type of surface modification (e.g., coatings or ion implantation) is employed.

Coefficients of friction for diamond, known to be one of the slipperiest materials, are similar to those of polytetrafluoroethylene in terrestrial environments (1). Natural diamond or high-pressure and high-temperature manufactured diamonds are available as three-dimensional products. However, the CVD diamond films and diamondlike carbon (DLC) films are available in a planar film or sheet and can be grown economically on ceramics such as $Si_3N_4$. Diamond and DLC films could offer tribologists and designers the combined properties of hard coatings and solid lubrication (2).

*In this investigation, fine-grain diamond, coarse-grain diamond,* and DLC were deposited on monolithic $Si_3N_4$ flat substrates. Reciprocating sliding-friction experiments were conducted with smooth flat surfaces of the diamond and DLC films in contact with hemispherical bare monolithic $Si_3N_4$ pins in humid air and in dry nitrogen. Comparative experiments for friction and wear were also conducted with bare surfaces of monolithic $Si_3N_4$ flats and a monolithic diamond (110) type IIa flat in contact with bare $Si_3N_4$ pins. Some earlier data and experimental details on this work and related research are given in references 3 to 9.

## 2. EXPERIMENT

### 2.1 Diamond and Diamondlike Carbon (DLC) Films

The as-deposited fine-grain diamond films were produced by a microwave plasma-enhanced CVD technique and are described in detail in references 3 and 4. The polished coarse-grain diamond films were produced by a hot-filament CVD technique and subsequently processed by diamond-wheel polishing. The deposition technique is described in detail in reference 9. The as-deposited DLC films, which are highly dense and pinhole-free, were produced by direct ion beam deposition from a Kaufman ion source (6).

A variety of techniques were used to characterize the diamond and DLC films. Scanning and transmission electron microscopy were used to determine surface morphology and to measure grain sizes. Surface profilometry was used to measure the surface roughness. Raman spectroscopy and Fourier transform infrared spectroscopy were used to characterize diamond quality and structure, while x-ray photoelectron spectroscopy (XPS) was used to characterize surface chemistry. Rutherford backscattering spectroscopy identified any impurities in the films and determined carbon and impurity concentrations. Proton recoil detection measured the hydrogen concentration and x-ray diffraction was used to determine the crystal orientation of the diamond films.

The physical characteristics of the diamond and DLC films are listed in table I. The average surface roughness of the two kinds of diamond and DLC films was small and ranged from 5 to 37 nm root-mean-square. The relatively smooth surface of the as-deposited fine-grain diamond, the polished coarse-grain diamond, and the as-deposited DLC films was attributed to the fine-grain microstructure, the diamond-wheel polishing, and the amorphous phase, respectively.

### 2.2 Friction and Wear Experiments

Reciprocating sliding friction experiments were conducted with the flats (i.e., diamond and DLC films, monolithic diamond (110) type IIa, and bare monolithic $Si_3N_4$) in contact with the bare monolithic $Si_3N_4$ pins in a humid air at a relative humidity of approximately 40 percent and in dry nitrogen. Details of the friction apparatus, the experimental procedures, and the wear measurements are described in reference 4; the experimental conditions are listed in table II. Hot-pressed, polycrystalline, magnesia-doped silicon nitride (92 $Si_3N_4$-4MgO-4$Y_2O_3$) was used as the flat and pin materials in the sliding friction experiments and as the substrate material for diamond and DLC films.

## 3. FRICTION AND WEAR PROPERTIES

Figure 1 presents coefficients of friction in humid air and dry nitrogen for the as-deposited fine-grain diamond film, the as-deposited DLC film, and the bare $Si_3N_4$ flat in sliding contact with the bare $Si_3N_4$ pins. The friction data indicate that the steady-state coefficient of friction was considerably lower for the as-deposited fine-grain diamond and as-deposited DLC films than for bare $Si_3N_4$ flat in humid air and dry nitrogen. Using a smooth diamond and DLC film with a $Si_3N_4$ substrate reduces the steady-state coefficient of friction to an acceptable level (e.g., $< 0.2$) in humid air and dry nitrogen. Note that the frictional results on the as-deposited fine-grain diamond and DLC films couple are consistent with those on the natural monolithic diamond (111) in humid air and dry nitrogen (5).

Generally, for the diamond film, the coefficient of friction decreased with an increase in the number of passes regardless of environment, reaching an equilibrium value after a certain number of passes. The high initial coefficients of friction observed for the as-deposited fine-grain diamond film in humid air and dry nitrogen predominantly resulted from the plowing or microcutting actions of some sharp edges of asperities present on the as-deposited fine-grain diamond film surface. As the sliding continued and the pin passed repeatedly over the same track, the tips of the sharp edges of asperities on the track quickly became dull and the coefficient of friction was appreciably affected by blunting the edges of asperities. Therefore, the coefficient of friction is markedly reduced in the initial stage of the experiment.

For the DLC film, the coefficient of friction was almost constant in a humid-air environment, but decreased with the increasing number of passes in dry nitrogen, reaching an equilibrium value. For the bare $Si_3N_4$ flat, the coefficient of friction increased with an increase in number of passes regardless of environment, reaching an equilibrium value after a certain number of passes. For the bare $Si_3N_4$ flat, the low initial coefficients of friction observed in humid air and dry nitrogen predominantly resulted from a contaminant layer formed on $Si_3N_4$ surfaces by the interaction of the surface with the environment.

Thin contaminant layers are unavoidably present on every surface of any solid that has been exposed to air or nitrogen. The layers are made up of contaminants such as adsorbed gases, water vapor, and hydrocarbons and have a thickness of atomic dimensions (around 2-nm thick). These contaminants can greatly reduce friction and accordingly provide lubrication as seen in the initial stage of the experiment. Under the repeated sliding, the contaminant surface layers are removed, thus, direct contact of the fresh surfaces is unavoidable. This situation applies to the sliding contact in the condition of steady-state (equilibrium) coefficient of friction for the $Si_3N_4$-$Si_3N_4$ couples (fig. 1b).

It is well known that sliding action in humid air increases the chemical reaction rate between $Si_3N_4$ and water vapor. Many researchers have found that the tribochemical interactions produce reaction products (i.e., silicon dioxide) and lead to a decrease in the coefficient of friction for the $Si_3N_4$-$Si_3N_4$ couple (e.g., 10). The frictional results for the bare $Si_3N_4$ flat shown in figure 1 are consistent with many researchers' findings. However, for the diamond and DLC films, the formation of silicon dioxide on the counterfacing $Si_3N_4$ pin in humid air leads to increases in the coefficient of friction. The presence of the silicon oxide layer on the bare $Si_3N_4$ pin plays a role in the relatively high friction process for the diamond and DLC films.

Figure 2 presents steady-state (equilibrium) coefficients of friction and wear rates in humid air and dry nitrogen for the as-deposited fine-grain diamond, polished coarse-grain diamond, and as-deposited DLC films, bare monolithic diamond (110) type IIa flat, and bare monolithic $Si_3N_4$ flat in contact with bare $Si_3N_4$ pins. The friction and wear data indicate conditions that reduce friction (e.g., a particular combination of environment and material) usually reduce wear rate as well.

The results presented in figure 2 demonstrate that the as-deposited fine-grain diamond, polished coarse-grain diamond, and DLC films improved both friction and wear properties of $Si_3N_4$. The steady-state coefficients of friction and the wear rates of the bare $Si_3N_4$ flat are high in humid air and dry nitrogen. On the other hand, all the as-deposited fine-grain diamond, polished coarse-grain diamond, DLC, and diamond (110) type IIa flat in contact with bare $Si_3N_4$ pins have a low steady-state coefficient of friction ($<0.2$) and a low wear rate ($10^{-7}$ $mm^3/N{\cdot}m$ or less). Those carbon films can be effective wear-resistant, self-lubricating films for ceramics.

## 4. CONCLUDING REMARKS

As-deposited fine-grain diamond, polished coarse-grain diamond, and as-deposited DLC films can be effectively used as wear-resistant, self-lubricating coatings for silicon nitride ($Si_3N_4$) in humid air and dry nitrogen. Those films (deposited on $Si_3N_4$ substrates) in sliding contact with bare $Si_3N_4$ pins in humid air at a relative humidity of 40 percent and in dry nitrogen have low steady-state coefficients of friction ($< 0.2$) and low wear rates ($< 10^{-7}$ $mm^3/N{\cdot}m$).

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TABLE I.—COMPARISON OF AS-DEPOSITED FINE-GRAIN DIAMOND, POLISHED COARSE-GRAIN DIAMOND, AND AS-DEPOSITED DIAMONDLIKE CARBON (DLC) FILMS

| Condition | As-deposited fine-grain diamond film | Polished coarse-grain diamond film | As-deposited DLC film |
|---|---|---|---|
| Composition | Essentially carbon, < 2.5 at % hydrogen | Essentially carbon | 70 at % carbon and 30 at % hydrogen |
| Microstructure | Polycrystalline | Polycrystalline | Amorphous |
| Crystal orientation | <110> | <111> | ---------- |
| Grain size, nm | 20 to 100 | 10 000 | ---------- |
| Raman spectrum | Sharp peak centered near 1330 $cm^{-1}$; broad humps centered near 1320 $cm^{-1}$ and in 1500 to 1530 $cm^{-1}$ range | Sharp peak centered near 1330 $cm^{-1}$; broad humps centered near 1320 $cm^{-1}$ and in 1500 to 1530 $cm^{-1}$ range | Broad peak at 1539 $cm^{-1}$; weak shoulder peak around 1340 $cm^{-1}$ |
| Atom-bonding state | $sp^3$ and $sp^2$ (variable ratio, very roughly 1:1) | $sp^3$ and $sp^2$ (variable ratio) | $sp^3$ and $sp^2$ |
| Surface morphology | Granulated or spherulitic: spherical asperities of different sizes | Flat, polished | Pinhole-free uniform smooth surface |
| Surface roughness, rms, nm | 6 to 37 | 6 to 25 | 5 |
| X-ray photoelectron spectroscopy (XPS) spectrum | Carbon and oxygen peaks | Carbon and oxygen | Carbon and oxygen |
| C/O ratios in XPS spectrum | 8 to 12 | 10 | ---------- |

TABLE II.—CONDITIONS OF SLIDING FRICTION EXPERIMENTS IN HUMID AIR AND DRY NITROGEN

[Pin specimens were polished with 3-μm diamond powder and 1-μm aluminum oxide powder, respectively. Hemispherical pin specimen radius, 1.6 mm.]

| | |
|---|---|
| Contact | Hemispherical pin on flat configuration |
| Load, N | 1 |
| Environment | Humid air (relative humidity 40 percent) and dry nitrogen (relative humidity less than 1 percent) |
| Temperature, °C | 23 |
| Motion | Unidirectional sliding |
| Sliding velocity, mm/min | 86 |
| Total passes | 30 000 |

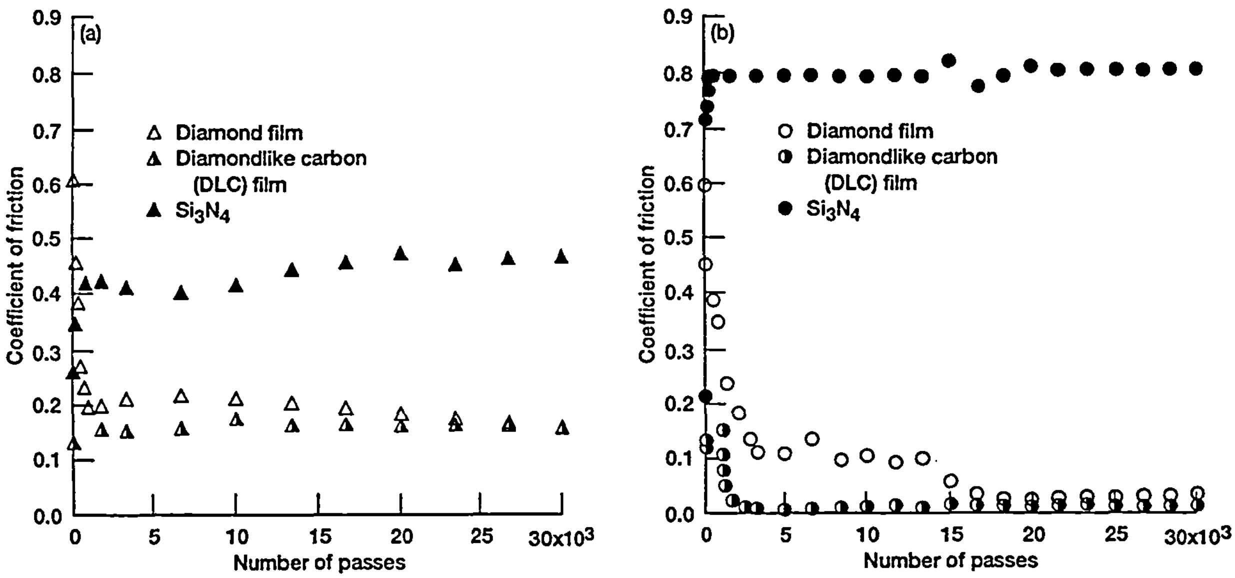


Figure 1.—Coefficients of friction for as-deposited fine-grain diamond film, as-deposited DLC film, and bare $Si_3N_4$ flat in contact with $Si_3N_4$ pins as function of number of passes. (a) Humid air. (b) Dry nitrogen.

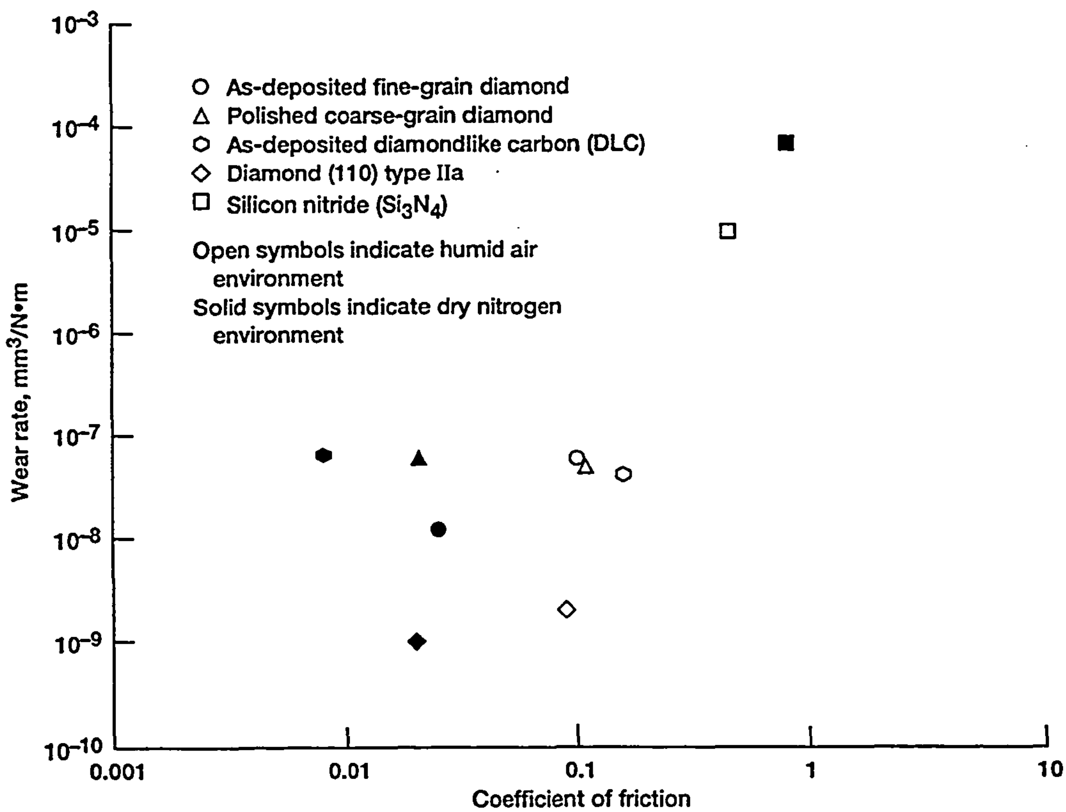


Figure 2.—Coefficients of friction and wear rates of as-deposited fine-grain diamond, polished coarse-grain diamond, as-deposited DLC, diamond (110) type IIa, and $Si_3N_4$ in contact with $Si_3N_4$ in humid air and dry nitrogen.

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